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⑤ A process for growing crystalline hydrous alumina within the pores of a porous substrate.

⑤ Porous substrates containing seeds of hydrous crystalline alumina are contacted with an aqueous solution of alkaline aluminate, thereby causing additional crystalline hydrous alumina to grow on the seeds within the pores of the substrate. Preferable substrates are macroporous ion-exchange resins.

EP 0 103 035 A1

A PROCESS FOR GROWING CRYSTALLINE HYDROUS ALUMINA
WITHIN THE PORES OF A POROUS SUBSTRATE.

It is known, e.g., from U.S. Patents 4,116,858
(Lee and Bauman, September 26, 1978) and 4,154,311 (Lee
and Bauman, June 26, 1979) that an ion-exchange resin may
be saturated with aqueous AlCl_3 solution and that reaction
5 with NH_4OH converts the AlCl_3 in situ to $\text{Al}(\text{OH})_3$. This
so-formed amorphous $\text{Al}(\text{OH})_3$ is then reacted with LiX ,
where X is halide, at elevated temperature to form crys-
talline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ which is useful in selectively recov-
ering Li^+ values from aqueous solutions, e.g., Li-contain-
10 ing brines.

It is also known, e.g., from U.S. Patents
4,116,856 (Lee and Bauman, September 26, 1978) and
4,221,767 (Lee and Bauman, September 9, 1980) that
improvements in the above discussed formation of crys-
15 talline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$ are found by reacting amorphous
 $\text{Al}(\text{OH})_3$ or crystalline hydrous alumina (e.g., nordstran-
dite, bayerite, gibbsite or mixtures of these) with LiOH
to form $\text{LiOH} \cdot 2\text{Al}(\text{OH})_3$ which is then reacted with LiX to
form the crystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3$, where X is halide.

Various forms of alumina, Al_2O_3 , are known, some of which occur as natural minerals, some of which are hydrated and some of which are crystalline. The Handbook of Chemistry shows the following:

5	<u>Name</u>	Crystalline	<u>M.P. °C</u>
		<u>Form</u>	
	aluminum oxide, Al_2O_3	hex. col.	2050
	$\alpha\text{-Al}_2\text{O}_3$, corundum	trig; col. cr, n	2015
	$\gamma\text{-Al}_2\text{O}_3$, γ -alumina	wh. micro. cr., n	tr. to alpha
10	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, gibbsite, (hydrargillite)	monocl., wh. cr.	tr. to $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Boehmite)
	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, bayerite	wh. micro. cr.	tr. to $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Boehmite)
15			
	aluminum oxide, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	amor. wh. pwd.	-x H_2O , tr. to $\gamma\text{-Al}_2\text{O}_3$

Nordstrandite is a crystalline hydrous alumina, as are gibbsite and bayerite.

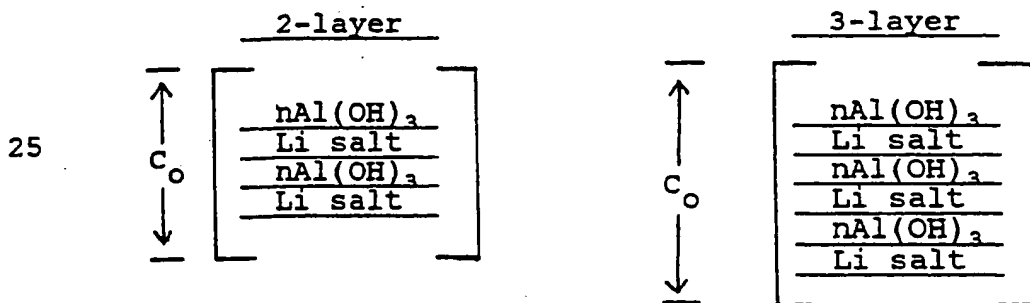
- 20 The present process differs from the above previous lithium aluminate preparations in that AlCl_3 is used only once, to provide amorphous $\text{Al}(\text{OH})_3$ in a substrate such as a macroporous ion-exchange resin. Further loading of Al into the substrate pores is accomplished by crystallizing the alumina in the pores and
- 25 growing the crystals in an alkaline aluminate solution.

The present invention is a process for growing crystalline hydrous alumina within the pores of a porous

substrate, characterized by providing a seed of crystalline hydrous alumina in said pores by the in situ precipitation of a water-soluble aluminum compound, thereby forming amorphous hydrous alumina; converting the so-formed
 5 amorphous hydrous alumina to crystalline hydrous alumina by heating; and adding to the seed-bearing substrate an aqueous solution of an alkaline aluminate, thereby providing aluminum oxide values which grow additional quantities of crystalline hydrous alumina on the crystalline hydrous alumina
 10 seeds.

The so-formed crystalline hydrous alumina may then be converted to $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ by reaction with a lithium salt, where X is an anion or negative valence salt radical. Depending on the type of crystalline hydrous
 15 alumina formed, the crystalline unit cells may be of the 2-layer or 3-layer variety.

As used herein, the expressions "2-layer" and "3-layer" refer to the number of layers bounded on both sides by the aluminate layers into which the subject Li
 20 compounds are intercalated. The following graphic illustrations will aid in describing the 2-layer and 3-layer systems:



It will be realized that the crystals of lithium aluminates are normally present as aggregates or stacks of a plurality of unit cells rather than each unit cell standing as a separate physical entity.

5 2-Layer $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ is formed from gibbsite and a lithium salt (LiX) other than LiOH. The lithium salt concentration must be high (at least about 12-15 percent of LiCl, for example) and the temperature must be high, preferably close to the boiling point of
10 the LiX solution. LiOH tends to solubilize the gibbsite and when it reprecipitates it forms 3-layer unit cells.

 3-Layer $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ is formed from hydrous alumina and LiOH which forms crystalline $\text{LiOH} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, which can then be neutralized with an acid to form crystal-
15 line $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, where X is the anion of the acid or of the lithium salt.

 The porous substrate into which the crystalline hydrous alumina is loaded may be an inert material, such as an inorganic or organic material. For certain
20 uses and reasons, the substrate is preferably a macroporous resin such as an ion-exchange resin as taught in U.S. Patents 4,116,858 and 4,116,856, both previously identified. Examples of the macroporous resins that can be employed are the strong acid and weak base types
25 of macroporous resins.

 Once the substrate is loaded to satisfaction with the crystalline hydrous alumina, the composite is then ready for reaction with LiX, where X is a monovalent anion, such as OH^- , Cl^- , Br^- , I^- , RCOO^- or OCl^- , or

may be divalent or trivalent, such as SO_4^{--} , PO_4^{---} or $\text{R}(\text{COO})_2^{--}$.

The alkaline aluminate solution, e.g., where x is a numerical value of 0.4 to 0.5 $\text{NaAlO}_2 \cdot x\text{NaOH}$, may be prepared, e.g., by dissolving commercial grade sodium aluminate, NaAlO_2 , in water or may be prepared, e.g., by reacting $\text{Al}(\text{OH})_3$ with concentrated NaOH . Commercially available solutions of sodium aluminate can be used. When reacting crystalline $\text{Al}(\text{OH})_3$ with concentrated NaOH it is preferred that the NaOH be of 50 percent concentration or higher, at a temperature at which the NaOH is a liquid. After the $\text{NaAlO}_2 \cdot x\text{NaOH}$ is prepared, it is diluted during its use in the present invention. When preparing the aluminate solution, it is also preferred that there be about 1.0 to 1.5 mole of NaOH per mole of $\text{Al}(\text{OH})_3$, since too much caustic tends to solubilize the crystalline hydrous alumina seed which is provided in the porous substrate to serve as precipitation sites for additional growth of crystalline hydrous alumina. The alkaline material may be KOH , but it is more costly.

In preparing a porous substrate having "seeds" of crystalline $\text{Al}(\text{OH})_3$ within the small pores, it is not generally possible or practical to insert appreciable amounts of non-soluble crystals into the pores. Therefore, the seeds are best implanted by providing aluminum solution in the pores and then precipitating hydrous alumina in situ within the pores. To accomplish this one may use a soluble Al salt, e.g., AlCl_3 , and then alkalize the Al to insoluble $\text{Al}(\text{OH})_3$. This freshly formed $\text{Al}(\text{OH})_3$, being amorphous, is then treated in one of various ways to cause the $\text{Al}(\text{OH})_3$ to crystallize.

When the substrate is a weak base anion-exchange resin in its basic form, the preferred procedure for incorporating $\text{Al}(\text{OH})_3$ seeds therein is to add an aqueous solution of AlCl_3 to where the amount of Cl^- is about equivalent to the base capacity. After about 1 hour at room temperature (or somewhat shorter times if the mixture is warmed to not more than about 60°C), most, if not all, of the Al values have been converted to $\text{Al}(\text{OH})_3$. This is followed by washing out excess AlCl_3 , titrating to the resin-OH capacity with NaOH and washing again to substantially remove remaining chlorides.

When the substrate is any other porous structure (other exchange resins, polymers or inorganic inert materials), it is recommended that the seeds be implanted within the pores by using soluble Al (such as AlCl_3) which is precipitated in situ using NH_4OH to form $\text{Al}(\text{OH})_3$ in the pores. Excess AlCl_3 , or $\text{Al}(\text{OH})_3$ formed outside the pores, is easily washed away.

Once the seed of $\text{Al}(\text{OH})_3$ is implanted in the pores of the substrate it may be conveniently crystallized as nordstrandite, bayerite or gibbsite, e.g., as follows:

1. To obtain nordstrandite use a soluble amine, e.g., ethylenediamine (about 20 percent concentration) at about 50°C overnight, then wash out the amine.
2. To obtain bayerite use NH_3 (about 1-30 percent in H_2O) at reflux temperature for 1-16 hours or more, then wash out excess NH_4OH .

3. To obtain gibbsite use aqueous NaOH in an amount of about 0.1-0.5 mole of NaOH per mole of $\text{Al}(\text{OH})_3$, boil for about 0.5 hour or more, and wash with H_2O . Sodium aluminate may be used instead of the NaOH.

5 Any of the above-described seeds of crystalline $\text{Al}(\text{OH})_3$ may be used as growth sites for producing additional crystalline $\text{Al}(\text{OH})_3$ by treatment with alkaline aluminate solution. If this additional treatment is done at less than about 50°C , the newly-precipitated
10 crystalline $\text{Al}(\text{OH})_3$ is principally nordstrandite and/or bayerite; if done at greater than about 50°C it is principally gibbsite. There is a tendency for the seed crystal to promote formation of additional $\text{Al}(\text{OH})_3$ having the same crystal structure as the seed.

15 The $\text{NaAlO}_2 \cdot x\text{NaOH}$, once formed, and having a $\text{NaOH}/\text{Al}(\text{OH})_3$ ratio generally in the range of about 1.0-1.5, is then preferably used as a diluted aqueous solution of about 5-30 percent concentration by weight as the precursor for the additional $\text{Al}(\text{OH})_3$ growth on the
20 seed. The $\text{NaAlO}_2 \cdot x\text{NaOH}$ solution is mixed with the seed-containing porous substrate. As the aluminum oxide in the sodium aluminate becomes crystallized to $\text{Al}(\text{OH})_3$, the pH increases. Addition of more amorphous aluminum hydroxide lowers the pH by reforming additional sodium
25 aluminate and solubilizes the amorphous alumina which then crystallizes out of the sodium aluminate and produces further growth of the seeded crystalline $\text{Al}(\text{OH})_3$ which is, again, indicated by a rise in the pH. The step of adding $\text{NaAlO}_2 \cdot x\text{NaOH}$, or of adding amorphous alumina to reform $\text{NaAlO}_2 \cdot x\text{NaOH}$, may be repeated one or more
30

times until the relative speed of pH change is slowed, indicating that the pores are substantially filled with crystalline $\text{Al}(\text{OH})_3$ and any additional formation of crystalline $\text{Al}(\text{OH})_3$ is likely to take place outside the pores.

5 If additional pre-formed $\text{NaAlO}_2 \cdot x\text{NaOH}$ is added as a source of additional crystalline $\text{Al}(\text{OH})_3$, it should be preceded by an amount of acid (preferably HCl) to neutralize the caustic already present from a previous addition of sodium aluminate. This prevents the caustic from building to a

10 concentration which would resolubilize the desired crystalline $\text{Al}(\text{OH})_3$.

Another technique for causing additional precipitation of hydrous alumina onto the seed, is to add the alkaline aluminate in an amount sufficient to supply

15 all, or even an excess, of the aluminate values expected to be precipitated. Then by slow or incremental addition of an acid, e.g., HCl , the alkaline metal is converted to alkali metal salt (e.g., NaCl), thus decreasing the ratio of alkali metal hydroxide in the alkaline aluminate,

20 thereby causing precipitation of the aluminate and causing the seed to add to this additional aluminate.

It can be seen, then, that by reacting amorphous aluminum hydroxide to form sodium aluminate, the amorphous aluminum hydroxide is solubilized. The solubilized amorphous aluminum hydroxide, in the presence

25 of the crystalline $\text{Al}(\text{OH})_3$ seed, precipitates out as crystalline $\text{Al}(\text{OH})_3$ and the seed increases in size.

The reaction of LiX (i.e., a lithium salt or lithium compound) with the crystalline hydrous alumina

30 is performed using an aqueous solution of the LiX and

employing, preferably, an elevated temperature. It is best if the LiX is a concentrated solution and the temperature is at or near the boiling point. Weak solutions of LiX and/or lower temperatures of reaction are less effective in obtaining a high degree of the desired intercalation in a reasonable length of time.

The term "intercalation" is used to indicate that the reaction of the LiX with the crystalline hydrous alumina hydroxide creates $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ crystals wherein the LiX moiety lies between layers of the hydrous alumina hydroxide and causes an expansion of the hydrous alumina crystal lattice. The LiX can be substantially leached out, but so long as a significant percentage of it remains, e.g., about 50 percent of the possible amount, the crystal lattice remains expanded and the amount of intercalated LiX can be replenished until the lattice is again loaded with LiX.

The advantages of the present method and of using $\text{NaAlO}_2 \cdot x\text{NaOH}$ as the source of hydrous alumina to build crystalline $\text{Al}(\text{OH})_3$ in the substrate are:

1. crystalline $\text{Al}(\text{OH})_3$ (such as gibbsite, bayerite, nordstrandite and mixtures of these) can, by being combined with NaOH, be used and the substrate substantially loaded with the crystalline material, using fewer steps than are shown in U.S. Patents 4,116,856 and 4,116,858 (both previously identified);

2. because it is not necessary to dry the substrate (such as an ion-exchange resin) after the first

loading step, osmotic shock is substantially decreased and substrate breakage or decrepitation is substantially avoided;

3. because the composite is neutralized only once, aluminum loss due to neutralization problems is minimized;

4. one may selectively prepare 2-layer lithium aluminates or 3-layer lithium aluminates; and

5. having the hydrous alumina present in the porous substrate as crystalline $\text{Al}(\text{OH})_3$ rather than amorphous $\text{Al}(\text{OH})_3$ is beneficial in providing optimum loading of LiX , thereby forming crystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ in a more consistent and expeditious manner.

Example 1

15 (a) Lithium Aluminate from Gibbsite

A macroporous strong acid ion-exchange resin (525 ml) containing 10 percent divinylbenzene is stirred into an equal volume of 29 percent aqueous AlCl_3 solution. The resin is filtered so that the excess AlCl_3 solution is removed from the resin. The resin is dried to free-flowing resin with dry N_2 and then stirred into 600 ml of aqueous 30 percent NH_3 solution. The mixture is washed. The resin is contacted with an excess of brine to convert RSO_3NH_4 to RSO_3Na and then filtered to remove all of the solution from the beads. The resin is then added to 456 g of H_2O and 230 g of $\text{NaAlO}_2 \cdot \frac{1}{2}\text{NaOH}$ solution

(from gibbsite and 50 percent NaOH). The mixture is stirred and heated to 75°C-80°C for one hour. The temperature is reduced to 70°C and five 25-g additions of amorphous $\text{Al}(\text{OH})_3$ are added at 10-minute intervals.

5 After the last addition, the heat and stirrer are turned off and the resin mixture is allowed to set overnight. The final aluminum content of the washed resin is approximately 3.92 mmoles of Al/ml of resin. X-ray diffraction analysis shows very crystalline gibbsite is present in

10 the resin.

(b) Conversion to 2-Layer Lithium Aluminate

The resin is refluxed in 30 percent aqueous LiCl solution for at least 4 hours. The resin now contains 2-layer $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$.

15 (c) Preparation of 3-Layer $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ in a porous substrate via gibbsite

The same resin employed in (a) (110 ml) and containing gibbsite, prepared as described above, is heated with 110 ml of an aqueous solution containing

20 8.31 g of LiCl and 3.52 g of $\text{LiOH} \cdot \text{H}_2\text{O}$. The resulting slurry is stirred at a temperature of 75°C. 1N NaOH (75 ml) are added and the resin is heated for another hour. The resin is placed in a 95°C oven for 12 hours. X-ray analyses of samples taken periodically show a

25 decrease in the amount of gibbsite with a corresponding increase in the amount of $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$.

The resin is then washed and neutralized with HCl in a solution containing NH_4Cl and LiCl . Neutralization to a pH of 5.6 (at room temperature) requires about 220 milliequivalents of HCl. The $\text{LiCl}\cdot\text{LiOH}\cdot\text{gibbsite}$ reaction will also take place at 25°C .

(d)

The same resin employed in (a) and (c) above (225 ml) and containing gibbsite (3.7 mmoles of Al/ml of resin) is placed in a stainless steel beaker with 275 ml of H_2O and 35 g of $\text{LiOH}\cdot\text{H}_2\text{O}$ and the mixture heated to 80°C . X-ray analysis shows that all of the gibbsite is converted to 3-layer $\text{LiOH}\cdot 2\text{Al}(\text{OH})_3\cdot n\text{H}_2\text{O}$ in about 30 minutes. The resin is neutralized with HCl. This reaction also occurs at room temperature but at a much slower rate.

Example 2

(a) Preparation of 3-Layer $\text{LiCl}\cdot 2\text{Al}(\text{OH})_3\cdot n\text{H}_2\text{O}$ in a Porous Substrate via Bayerite

A macroporous weak base ion-exchange resin (500 ml) in the chloride form is poured into an equal volume of saturated aqueous AlCl_3 solution. The slurry is stirred without heating for 40 minutes. The resin is filtered by suction until all of the excess AlCl_3 solution is removed from the resin and the resin is stirred into 500 ml of 30 percent NH_3 in H_2O at room temperature. An exotherm from 25°C to 30°C is observed. The resin is stirred for a total of 20 minutes. The ammonia solution is poured off of the resin and the resin is allowed to set for 16 hours at room temperature. X-ray analysis of

the resin shows that bayerite has formed in the resin. There is still a large amount of amorphous $\text{Al}(\text{OH})_3$ present. Aluminum analysis indicates that the resin contains 0.7 mmole of Al/ml of resin at this point.

- 5 The resin is washed thoroughly so that the filtrate is clear. Even a small amount of crystalline $\text{Al}(\text{OH})_3$ in the solution phase cannot be tolerated.

- The resin and 230 ml of deionized water are stirred and heated to 45°C and 173 g of freshly prepared
10 $\text{NaAlO}_2 \cdot x\text{NaOH}$ is added to the slurry. This mixture is reacted for 1 hour. From x-ray data it can be seen that the amorphous $\text{Al}(\text{OH})_3$ content of the resin is decreased.

- Four 216-g additions of amorphous $\text{Al}(\text{OH})_3$ are added at 15-minute intervals. After the last addi-
15 tion, the resin is allowed to stand for 16 hours. X-ray analysis of the product shows only well crystallized bayerite.

(b)

- The resin described above (210 ml) is neutralized with 240 milliequivalents of HCl . The resin is
20 then heated at 110°C - 115°C in 250 ml of 30 percent LiCl solution for 1.5 to 3 hours. Very crystalline 3-layer $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ is the product. No further neutralization is necessary.

- 25 Bayerite in porous resin can also be converted to 3-layer lithium aluminate by reaction with LiOH or a mixture of LiCl and LiOH .

Example 3 - Growth of Nordstrandite in a Porous Substrate

The same resin employed in Example 2 (500 ml) is poured into an equal volume of aqueous 25 percent AlCl_3 solution and the mixture is stirred for 30-40 minutes. The resin is then filtered to remove the excess AlCl_3 and stirred into 30 percent NH_4OH solution. The resin is stirred for 30 minutes and washed thoroughly with H_2O . The resin is successively treated with NH_4OH and H_2O until substantially all of the Cl^- is removed. The resin is washed with deionized water to remove all traces of NH_4OH .

The resin is then placed in a polyethylene bottle with an equal volume of 12 percent ethylenediamine and heated at 50°C for 16 hours. X-ray shows the presence of nordstrandite.

The resin is then contacted with an equal volume of deionized water and 230 g of fresh $\text{NaAlO}_2 \cdot \frac{1}{2}\text{NaOH}$ for one hour. Five 25-g additions of amorphous $\text{Al}(\text{OH})_3$ are then added at 15-minute intervals. The resulting product is nordstrandite in the pores of the resin.

Example 4 - The Modified Method for High Loading of Crystalline Hydrous Alumina

To 3000 ml of the same resin employed in Examples 2 and 3 except that it was in the OH^- form, was added water to a total of 3750 ml was stirred as 147 g of anhydrous AlCl_3 were added. Stirring was continued for one

hour as the pH slowly rose to 5. The slurry was well washed with deionized water until the effluent was almost colorless. The washed resin was reslurried with 40 ml of 30 percent NH_3 and 155 ml of 50 percent NaOH to a pH of 10.5. The resin was then washed on a filter.

A sample of 197 ml of the resin so prepared was slurried in H_2O with 5.22 g of $\text{NaAlO}_2 \cdot x\text{NaOH}$ ($\text{NaAlO}_2 \cdot x\text{NaOH}$ is a solution of sodium aluminate made by dissolving 1960 g of gibbsite in 2100 ml of 50 percent NaOH at 100°C). The final volume of resin was 192 ml.

The resin was transferred to a one-liter beaker and 299 g of $\text{NaAlO}_2 \cdot x\text{NaOH}$ was added plus water to a total volume of 540 ml. By means of a pump, 36 percent HCl was metered into the stirred slurry at a rate of 1 ml/minute. The temperature rose to a maximum of 40°C and it was maintained at 30°C - 40°C during the course of the HCl addition. The pH decreased from 14 to 12.8. The pump was controlled by the pH, and near the end of the HCl addition, was essentially in an on-off mode as the pH fluctuated. After 164 ml of 35 percent HCl had been added the slurry was well washed to yield 230 ml of resin which contained 4.63 mmoles of Al/cc of resin. The Al was present as bayerite as determined by x-ray.

25 Example 5

The same resin employed in Examples 2 and 3 (200 ml) was treated at room temperature with a large excess of aqueous 25.5 percent AlCl_3 . The resin is sucked dry on a filter funnel and dumped into 200 ml of

30 percent aqueous ammonia and stirred for 15 minutes. The resin is rinsed briefly with water and allowed to stand overnight at room temperature. It was titrated to stable 10.1 pH with 74 ml of N/1 NaOH. The resin
5 was then washed until chloride free to give a settled volume of 166 ml and was added to water to a total volume of 260 ml. A sodium aluminate solution (4.4 g) (1960 g of gibbsite dissolved in 2100 ml of 50 percent NaOH at 100°C) was added. After one hour of stirring
10 at room temperature an additional 70 g of sodium aluminate solution was added. After an additional 45 minutes of stirring at 30°C-35°C, the pH had risen to 13.6. During the next hour four equal additions of amorphous $\text{Al}(\text{OH})_3$ (100 g \approx 1 mole Al) of 9 g each were made. The
15 pH held at 13.5-13.6. The supernatant solution was filtered and returned to the resin pot with a pH increase to 13.9. Two more 9-g additions of amorphous $\text{Al}(\text{OH})_3$ were made during the next hour and then two more 9-g additions in the next 45 minutes. The washed resin,
20 with a settled volume of 203 ml, showed an aluminum content of 4.5 mmoles/ml.

Claims

1. A process for growing crystalline hydrous alumina within the pores of a porous substrate, characterized by providing a seed of crystalline hydrous alumina in said pores by the in situ precipitation of a water-soluble aluminum compound, thereby forming amorphous hydrous alumina; converting the so-formed amorphous hydrous alumina to crystalline hydrous alumina by heating; and adding to the seed-bearing substrate an aqueous solution of an alkaline aluminate, thereby providing aluminum oxide values which grow additional quantities of crystalline hydrous alumina on the crystalline hydrous alumina seeds.

2. The process of Claim 1 wherein the alkaline aluminate comprises $\text{NaAlO}_2 \cdot x\text{NaOH}$ where x is a numerical value of 0.1 to 0.5.

3. The process of Claim 1 wherein the production of the additional quantities of crystalline hydrous alumina is promoted by addition of an acid which forms a soluble salt with the alkali.

4. The process of Claim 3 wherein the acid is HCl.

5. The process of Claim 1 wherein the porous substrate is selected from the group consisting of inorganic, organic, polymeric and resinous materials.

6. The process of Claim 1 wherein the porous substrate is a macroporous ion-exchange resin.

7. The process of Claim 1 and including the additional step of reacting the so-formed crystalline hydrous alumina with LiOH to form crystalline $\text{LiOH} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$.

8. The process of Claim 1 and including the additional step of reacting the so-formed crystalline hydrous alumina with lithium salt, LiX, to form crystalline $\text{LiX} \cdot 2\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ where X is the anion of the lithium salt.



European Patent
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EUROPEAN SEARCH REPORT

0103035
Application Number

EP 82 10 8327

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-A-4 348 296 (W.C. BAUMAN et al.) -----	1-8	C 01 D 15/00 C 01 F 7/00 B 01 J 41/08
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 01 D 15/00 C 01 F 7/00 B 01 J 41/00 B 01 J 47/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 02-05-1983	Examiner KESTEN W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, r after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EUROPEAN PATENT APPLICATION

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A method for producing zeolite-containing particles.

A method for producing zeolite-containing particles, in which the zeolite has a silica to alumina mole ratio of at least 12, comprises initially compositing seed crystals of the desired zeolite with a matrix material, such that said seed crystals comprise from 0.01 to 2.0 wt. percent of said matrix material, and then preforming the matrix material containing the said seed crystals into particles. The pre-formed particles are then contacted at a temperature of 60°C to 250°C with zeolite producing reactants comprising an alkaline aqueous solution in order to crystallize the required zeolite within said pre-formed particles, the weight ratio of the aqueous solution to said pre-formed particles being from 0.1 to 50, and the pH of the solution being in excess of 7. The resultant particles contain from 3% to 60% of the required zeolite.

A METHOD FOR PRODUCING ZEOLITE-CONTAINING PARTICLES

This invention relates to a method for producing zeolite-containing particles.

Crystalline zeolites have been prepared from mixtures of oxides including sodium oxide, alumina, silica and water. More recently clays and coprecipitated aluminosilicate gels, in the dehydrated form, have been used as sources of alumina and silica in zeolite reaction systems.

Seeding is a recognized method of initiating crystallization in zeolite synthesis. Generally in seeding, a small quantity of the desired product is injected into a suitable reaction mixture and, with good mixing, these crystals are circulated to provide nucleation sites for the formation of the net product. U.S. Patent No. 3,671,191 teaches a general seeding technique.

Most commonly, zeolite crystals are incorporated with a binder, i.e. a matrix, to form a catalyst or adsorbant particle. Such matrix is useful not only as a binder, but also to impart greater temperature and impact resistant to the catalyst.

It is recognized in the art that pre-formed catalyst matrix particles can also be transformed under certain conditions into zeolites. The use of matrices to form zeolites is described in many patents including U.S. Patent Nos. 3,746,659; 3,752,772; 3,773,391; 3,694,152; 3,663,456; 3,650,687; 3,647,718; 3,642,662 and 3,545,921. The most common matrix material used in the prior art to form zeolites is a clay, especially kaolin clay.

U.S. Patent 4,091,007 describes an improved method for preparing ZSM-5 by crystallizing a reaction mixture including clay as the major source of alumina, an added source of silica, water and an added source of cations.

The use of pre-formed and high clay content matrix particles places special restrictions on subsequent zeolite crystallization. When clays are used exclusively, the matrix particles tend to be fairly high in aluminum content. Another problem in the use of matrix particles is the tendency for these particles to serve simply as a source of nutrients for crystallization quite exterior to, and physically independent of the original matrix.

It is an object of this invention to furnish a method of fixing siliceous zeolite crystals in a pre-formed matrix. It is further object of the present invention to grow zeolite crystals within a pre-formed matrix, thus forming a matrix-containing zeolite which can be readily used as a catalyst or adsorbant particle. It will be appreciated that whereas conventional techniques for the manufacture of bound zeolite particles comprise two general steps, namely zeolite formation and then incor-

poration of said zeolite in a matrix, the present method allows these two general steps to be combined into a single operation with the attendant benefits of shorter zeolite crystallization time, higher zeolite yields and lower catalyst/adsorbent manufacturing costs. An unexpected result of the present method is the unique morphology and crystal size of the resulting zeolite particles.

In accordance with the present invention, there is now provided a method for producing zeolite-containing particles, in which the zeolite has a silica to alumina mole ratio of at least 12, the method comprising the steps of compositing seed crystals of the desired zeolite with a matrix material, such that said seed crystals comprise from 0.01 to 2.0 wt. percent of said matrix material, preforming said matrix material containing said seed crystals into particles and then contacting said pre-formed particles under reaction conditions including a temperature of from 60°C to 250°C with zeolite producing reactants comprising an alkaline aqueous solution to form a reaction mixture in order to crystallize said zeolite within said pre-formed particles, the weight ratio of said aqueous solution to said pre-formed particles being from 0.1 to 50, and the pH of said reaction mixture being in excess of 7, and recovering said particles containing from 3% to 60% of said zeolite.

Thus the present invention provides a method of producing siliceous zeolite crystals, i.e. having a silica to alumina mole ratio of at least 12, within a pre-formed matrix. This is accomplished by depositing seed crystals of the desired zeolite in the pre-formed matrix and then contacting the product with a zeolite forming mixture. Since circulation of the seed crystals cannot occur (since these seed crystals are fixed and imbedded within the matrix), it would seem at first glance that they would not be effective in promoting the crystallization of zeolites. Surprisingly, however, it is found that these imbedded seed crystals are effective in accelerating crystallization of zeolites.

The crystalline zeolites produced by the present method are members of a unique class of zeolitic materials which exhibit unusual properties. Although these zeolites have unusually low alumina contents, i.e. high silica to alumina mole ratios, they are very active even when the silica to alumina mole ratio exceeds 30. The activity is surprising since catalytic activity is generally attributed to framework aluminum atoms and/or cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam at high temperature which

induces irreversible collapse of the framework of other zeolites, e.g. of the X and A type. Furthermore, carbonaceous deposits, when formed, may be removed by burning at higher than usual temperatures to restore activity. These zeolites, used as catalysts, generally have low coke-forming activity and therefore are conducive to long times on stream between regenerations by burning carbonaceous deposits with oxygen-containing gas such as air.

With pure zeolite samples, the silica to alumina mole ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred in some applications to use zeolites having higher silica/alumina ratios of at least about 30. In addition, zeolites having very little aluminum, i.e. having silica to alumina mole ratios of 1,600 and higher, are found to be useful and even preferable in some instances.

An important characteristic of the crystal structure of certain zeolites in this unique class of zeolites is that they exhibit selective constrained access to and egress from the intracrystalline free space by virtue of having an effective pore size intermediate between the small pore Linde A and the large pore Linde X, i.e. the pore windows of the structure are of about a size such as would be provided by 10-membered rings of silicon atoms interconnected by oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline zeolite, the oxygen atoms themselves being bonded to the silicon (or aluminum, etc.) atoms at the centers of the tetrahedra.

Such preferred zeolites have an effective pore size such as to freely sorb normal hexane. In addition, the structure should provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the preferred type. Windows of 10-membered rings are preferred, although in some instances excessive puckering of the rings or pore blockage may render these zeolites ineffective. Al-

though 12-membered rings in theory would not offer sufficient constraint, it is noted that the puckered 12-ring structure of TMA offretite shows some constrained access.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access to molecules of larger cross-section than normal paraffins, a simple determination of the "Constraint Index" of the zeolite may be made as described in, for example, U.S. Patent No. 4016218. Preferred zeolites for use in the present method have a Constraint Index of 1 to 12.

Examples of such preferred zeolites are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38, with ZSM-5 being especially preferred. ZSM-5 is described in greater detail in U.S. Patents No. 3,702,886, Re. No. 29,948, No. 4,139,600 and No. 4,100,262. ZSM-11 is described in greater detail in U.S. Patents No. 3,709,979 and No. 4,108,881. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent Nos. 4,016,245 and No. 4,107,195. ZSM-38 is more particularly described in U.S. Patent No. 4,046,859.

Useful matrix materials for the pre-formed matrix of the present method include both synthetic and naturally occurring substances, as well as inorganic materials such as clay, silica, and/or metal oxides. The metal oxides may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Non-limiting examples of such porous matrix materials include silica, silica-alumina, silica-thoria, silica-magnesia, silica-zirconia, silica-beryllia and silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia.

Clay materials for use as matrix materials in the present invention include compositions composed primarily of clay minerals identified as hydrated aluminum silicates. Said hydrated aluminum silicate clay mineral may have associated therewith one or more metal or metal oxides selected from the group consisting of Group IA, IIA and VIII of the Periodic Table of the Elements (Sargent-Welch Company, 1968). Non-limiting examples of such hydrated aluminum silicate minerals which comprise the major proportion of clays for use in this invention include kaolinite, halloysite, montmorillonite, illite and attapulgite. Clays containing these minerals are represented by such non-limiting examples as fuller's earth (containing attapulgite with

some montmorillonite), kaolin (constituted of mainly kaolinite) and bentonite (containing appreciable amounts of montmorillonite and usually having some magnesium and iron associated therewith).

Only a small amount of zeolite seeds are needed for the present method, namely 0.01% by to 2.0% of seeds by weight of the matrix. It is preferred to use from about 0.1% to 1.0% of seeds by weight of the matrix. The seed used depends on the zeolite desired to be produced. For example, ZSM-5 seeds produce ZSM-5 zeolite and ZSM-11 seeds produce ZSM-11 zeolite.

It is preferred to form the seeded matrix particles by intimately admixing seed crystals with an inorganic oxide matrix while the latter is in a hydrous state (slurry-type material) such as in the form of a hydrosol, hydrogel, wet gelatinous precipitate, or a mixture thereof. If a hydrosol is formed, it can be permitted to set in mass to form a hydrogel which can thereafter be shaped, dried or spray-dried by conventional techniques. Alternatively, extrusion or pelletizing can be employed to form discrete particles. Once the particle is formed, its dimensions and geometry will be essentially fixed and will not be subject to substantial change during crystallization of the zeolite.

The seeded matrix particles are then contacted with a zeolite forming mixture under the proper reaction conditions to crystallize the desired zeolite within the matrix. In particular, the seeded matrix particles are contacted with an alkaline aqueous forming solution such that the weight ratio of said aqueous solution to said particles is between 0.1 and 50, preferably between 1.0 and 10. Hydroxide concentration in the initial forming solution will in general, be between 0.01 and 3.0 molar, preferably between 0.1 and 2.0 molar so as to ensure a final pH of solid-solution mixture in excess of 7.0. Preferably, the seeded matrix particles are contacted with the zeolite forming mixture without undergoing an initial calcination step.

Conventional zeolite forming mixtures are employed and comprise sources of an alkali metal oxide, e.g. a sodium oxide, an oxide of silicon (silica), an oxide of aluminum (alumina), water, and, if desired, a source of an organic nitrogen containing cation, such as an amine or diamine; e.g., butylamine, pentanediamine, hexanediamine; a tetraalkylammonium compound, e.g. a tetramethylammonium compound, a tetraethylammonium compound, a tetrabutylammonium compound, or a tetrapropylammonium compound; an

alkylenediamine, e.g. polymethylenediamine; pyridine or a tetraureacobalt (II) complex. In preparation of "extremely highly siliceous" zeolites such as those disclosed in U.S. Patent Re. No. 29,948, no source of an oxide of aluminum is employed in the reaction mixture.

The matrix material may also serve as a source of reactants. Thus the matrix may supply all or some of the required silica, alumina, or alkali metal. Additionally the matrix material may contain a zeolite with a silica to alumina mole ratio of less than 12, e.g. a synthetic faujasite type zeolite.

Generally, organic compounds will be present in the initial forming solution in a concentration of between 0.01 and 2.0 molar, preferably between 0.05 and 1.0 molar.

Crystallization is performed either at atmospheric pressure or under elevated pressure in an autoclave or static bomb reactor at pressures in the range of between 100 to 6080 kPa (1 and 60 atmospheres.) Crystallization is generally carried out at a temperature of 60°C to 250°C, but at lower temperatures in this range, e.g. below about 100°C, crystallization time is longer. Typical reaction conditions comprise maintaining the reaction mixture and the seeded matrix at a temperature of 80°C to 200°C for 1 hour to 60 days, more preferably at a temperature of 95°C to 160°C for 3 hours to 14 days. Thereafter, the matrix particles containing the crystallized zeolite are separated from the liquid and recovered.

Separation is conveniently effected by cooling the entire mixture to room temperature and then filtering and water washing the solid product. The product so obtained is dried, e.g. at 110°C, for from 1 hour to 8 hours. If desired, milder conditions may be employed, e.g. room temperature under vacuum. The final product is a matrix containing 3% to 60%, preferably 5% to 40% of the required zeolite, with the remainder being the matrix. The final product exhibits unexpected morphology and crystal size.

The following examples will serve to illustrate the invention.

EXAMPLE 1

Two clay-containing catalyst matrices were spray-dried in side-by-side experiments, one containing 1% ZSM-5 crystals, the other containing none. They analyzed as follows:

	<u>With crystals</u>	<u>Without</u>
$\text{SiO}_2/\text{Al}_2\text{O}_3$	5.31	5.70
Surface area (m^2/g),	204	220

No ZSM-5 was detected by X-ray diffraction in either material. The same clay-containing catalyst matrices utilized in Example 1 were employed in the following Examples 2 to 8. The matrix containing the crystals is referred to as "spray-dried, seeded material" and the matrix without crystals is referred to as "unseeded material".

EXAMPLE 2

Twenty grams of spray-dried, seeded material was combined with a solution of 0.20 g NaOH, 1.33 g TPABr and 2.58 g NaBr in 20 g water. The mixture was placed in a steam chest at 95°C. After one week, X-ray diffraction showed the solid to contain 35% ZSM-5. When the same treatment was given to the unseeded material, the solid contained only 15% ZSM-5. Thus the seeded material gave a greater zeolite yield than the unseeded material.

To show that the 35% ZSM-5 sample was not just a physical mixture of crystals with matrix particles, the sample was separated on a 200 mesh-screen. The portion passing through 200 mesh analyzed 35% ZSM-5; that retained, 38%.

EXAMPLE 3

Twenty grams of seeded material was treated as in Example 2 except that 40 g water was used. After 1 week, the solid contained 30% ZSM-5 whereas the unseeded material had only 10%.

EXAMPLE 4

Twenty grams of spray-dried, seeded material was combined with a solution of 2.04 g of 25% TPA hydroxide in 19 g water. The mixture was placed in a steam chest at 95°C. After one week, X-ray diffraction showed the solid to contain 30% ZSM-5. When the same treatment was used on unseeded material, the solid contained only 20% ZSM-5.

EXAMPLE 5

Eighty grams of spray-dried, seeded material was combined with a solution of 0.8 g NaOH, 10.3 g NaBr and 5.3 g TPABr in 80 g water. The mixture was placed in a 300 cc stainless steel autoclave and heated 4 hours at 160°C with slow stirring.

After cooling, filtering and drying, the product solid contained 16% ZSM-5. When the same treatment was employed with unseeded material, the solid contained only 2% ZSM-5.

EXAMPLE 6

Example 5 was repeated, but with 0.4 g NaOH, 5.3 g TPABr and no NaBr. After 6 hours at 160°C, the seeded material contained 15% ZSM-5; the unseeded sample contained only 2% ZSM-5.

EXAMPLE 7

Example 5 was repeated, but with 120 g solid, 1.2 g NaOH, 7.95 g TPABr and 60 g H₂O. After 6 hours at 160°C, the seeded material contained 15% ZSM-5; the unseeded sample contained only 3% ZSM-5.

EXAMPLE 8

This Example will serve to illustrate the necessity of alkalinity. The experiment of Example 5 was repeated, but with no NaOH. After 6 hours at 160°C, no crystallinity was found in either the seeded or unseeded matrix.

EXAMPLE 9

This example shows that the procedures of this invention would not destroy a synthetic faujasite type zeolite if it were present in the precursor composite. 40 grams of NaY were combined with 80 g water and 16.2 g 25% TPA OH. After 6 hours in an autoclave at 160°C, the solid was filtered and dried. X-ray analysis showed it to be 100% NaY.

Claims

1. A method for producing zeolite-containing particles, in which the zeolite has a silica to alumina mole ratio of at least 12, the method comprising the steps of compositing seed crystals of the desired zeolite with a matrix material, such that said seed crystals comprise from 0.01 to 2.0 wt. percent of said matrix material, preforming said matrix material containing said seed crystals into particles and then contacting said pre-formed particles under reaction conditions including a temperature of from 60°C to 250°C with zeolite producing reac-

tants comprising an alkaline aqueous solution to form a reaction mixture in order to crystallize said zeolite within said pre-formed particles, the weight ratio of said aqueous solution to said pre-formed particles being from 0.1 to 50, and the pH of said reaction mixture being in excess of 7, and recovering said particles containing from 3% to 60% of said zeolite.

2. The method of claim 1 wherein the amount of seed crystals comprise is between 0.1 and 1.0 wt. percent of the matrix.

3. The method of claim 1 or claim 2 wherein said zeolite is selected from the group ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38.

4. The method of any preceding claim wherein said reactants comprise sources of an alkali metal oxide, an oxide of silicon, water, and organic nitrogen-containing cations.

5. The method of claim 4 wherein said reactants further comprise a source of an oxide of aluminum.

6. The method of claim 4 or claim 5 wherein said

matrix serves as a source of an oxide of silicon, of an alkali metal oxide and/or of an oxide of aluminum.

5 7. The method of claim 1 wherein the pre-formed matrix is prepared from a clay.

8. The method of any preceding claim wherein said reaction conditions include a pressure of between 100 and 6080 kPa (1 and 60 atmospheres) and a contact of time of between 1 hour and 60 days.

9. The method of any preceding claim wherein said pre-formed particles are contacted with said zeolite producing agents without an intervening heat treatment step on the particles.

10. A process for converting feedstock comprising hydrocarbon compounds to product comprising hydrocarbon compounds of lower molecular weight than the feedstock hydrocarbon compounds which comprises contacting said feedstock at conversion conditions with a catalyst comprising an active form of zeolite-containing particles produced by a method of any preceding claim.

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European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 86303222.3

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE - A1 - 3 028 785 (ENGELHARD MINERALS & CHEMICALS CORP.) * Claims 1,6,9; page 13, lines 3-19; page 14, lines 7-34 * --	1,7,10	C 01 B 33/28 B 01 J 29/28 C 10 G 11/05 C 10 G 49/08
A	DE - A1 - 3 347 123 (W.R.GRACE & CO.) * Claim. 1; page 40, lines 24-35; page 41, lines 1-18 * --	1	
A	DE - A1 - 2 909 929 (BASF AG) * page 2, lines 1-9 * --	1,4	
A	US - A - 4 468 475 (MOBIL OIL CORP.) * Claims * --	1,5	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP - A1 - 0 134 333 (MOBIL OIL CORP.) * Claims * ----	1,5	B 01 J C 01 B
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 13-08-1986	Examiner PILLERSTORFF
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

